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ORIGINAL ARTICLE

Conjugation of diisocyanate side chains to dimethacrylate reduces polymerization shrinkage and increases the hardness of composite resins

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KEYWORDS
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urethane-modified resin

Background/Purpose: Polymerization shrinkage is one of the main causes of dental restoration failure. This study tried to conjugate two diisocyanate side chains to dimethacrylate resins in order to reduce polymerization shrinkage and increase the hardness of composite resins.
Methods: Diisocyanate, 2-hydroxyethyl methacrylate, and bisphenol A dimethacrylate were reacted in different ratios to form urethane-modified new resin matrices, and then mixed with 50 wt.% silica fillers. The viscosities of matrices, polymerization shrinkage, surface hardness, and degrees of conversion of experimental composite resins were then evaluated and compared with a nonmodified control group.
Results: The viscosities of resin matrices increased with increasing diisocyanate side chain density. Polymerization shrinkage and degree of conversion, however, decreased with increasing diisocyanate side chain density. The surface hardness of all diisocyanate-modified groups was equal to or significantly higher than that of the control group.
Conclusion: Conjugation of diisocyanate side chains to dimethacrylate represents an effective means of reducing polymerization shrinkage and increasing the surface hardness of dental composite resins.

Conflicts of interest: The authors have no conflicts of interest relevant to this article.

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Introduction

Composite resins are currently the most popular dental restorative materials worldwide. Composite resins provide certain advantages such as good esthetics, easy application, and lower costs. However, there remain some disadvantages to their use, such as polymerization shrinkage, low wear resistance, and marginal discoloration. Composite resins are composed of organic monomers and inorganic fillers. High molecular weight dimethacrylate monomers with low polymerization shrinkage and high strength, such as bisphenol A-glycidyl dimethacrylate (bis-GMA), are most commonly used. The high viscosity of bis-GMA reduces the loading of fillers and also the degree of conversion of the monomers in the absence of other low viscosity diluents.[1] Low molecular weight diluent monomers, such as triethylene glycol dimethacrylate, are often added to reduce viscosity and increase the reactivity and conversion rate.[1] However, the diluent monomers also increase polymerization shrinkage,[2] leading to polymerization stress, debonding at the restoration—tooth interface, secondary caries, postoperative sensitivity, pulpal irritation, and marginal discoloration.[3]

Polymerization shrinkage is the principal cause of failure of clinical dental composite resin fillings. Reducing this shrinkage, thus, represents one of the most important goals in the development of new matrices for composite resins. Investigators have made several efforts to achieve this goal, such as by adding inorganic inert fillers to reduce the volume of the matrix and, therefore, the polymerization shrinkage.[4] However, the viscosity of the resin matrix can limit filler loading. Jeon et al[5] synthesized a low-viscosity matrix by substituting the alkoxy for hydroxyl groups in bis-GMA to minimize the amounts of diluent monomers and the shrinkage. Jingwei et al[6] developed a new matrix with multibranches or multifunctional groups. However, resin matrices with multibranches or multifunctional groups display high viscosity and a low degree of conversion.

Currently, there remains a lack of "non-shrinkage" composite resins worldwide. In this study, we aimed to develop low-shrinkage composite resins for dental application. As expected, the higher the molecular weight and volume of the monomer, the less extensive the shrinkage when polymerized. Most commercial dental composite resins are composed of bis-GMA or its derivatives. We increased the molecular weight and volume of the dimethacrylate molecule by conjugating functional side chains to the dimethacrylate structure. Urethane, which is a compound of diisocyanate and 2-hydroxyethyl methacrylate (HEMA), is a material suitable for use as a bis-GMA side chain. Polyurethane displays certain advantages, such as low shrinkage, high wear resistance, and good biocompatibility. We selected two diisocyanates with different chemical structures as side chain materials: 4,4′-diisocyanatodicyclohexylmethane (H_{12}MDI) and toluene 2,4-diisocyanate (TDI). H_{12}MDI contains two aliphatic rings (cyclohexane) linked by a methyl group, whereas TDI contains a toluene moiety. When conjugated to dimethacrylate, these two chemical structures reduced polymerization shrinkage and increased the mechanical strength of the composites. Different structures and numbers of side chains on dimethacrylate provided different results.

The hypothesis tested in this study was that monomers with higher molecular weight and steric hindrance (side chains on dimethacrylates) would display lower polymerization shrinkage and higher mechanical strength. In this study, we conjugated diisocyanate and HEMA side chains, in various proportions, to bisphenol A dimethacrylate (DM) to synthesize urethane-modified dimethacrylate composite resins, with the aim of reducing polymerization shrinkage because of the relatively high molecular weight and cohesive energy density of the urethane group. We also evaluated the effects of different diisocyanate side chain structures and densities on the dimethacrylate resin composites.

Materials and methods

Preparation of multifunctional dimethacrylate composite resins

TDI (T, 2 equivalents; Acros Chemical Co., Geel, Belgium) and H_{12}MDI (H, 2 equivalents; Acros Chemical Co.) were poured into separate reaction bottles and HEMA (1 equivalent; Acros Chemical Co.) was then added to each bottle dropwise. Dry nitrogen gas was continuously purged during the reaction procedure to remove oxygen and moisture. A Fourier transform infrared (FTIR) spectrometer was used to monitor the peak of the isocyanate group (NCO—). When the peak intensity of NCO— had reached half of its original value, this indicated that the hydroxyl group (OH—) of HEMA had fully reacted with the isocyanate group (NCO—) of TDI or H_{12}MDI. Bisphenol A DM (Double Bond Chemical Ind. Co. Ltd., Taipei, Taiwan) was then added to the reaction mixtures as 4, 2, 1, or two-thirds equivalents in the nitrogen atmosphere. When the peak of the isocyanate group had disappeared, this indicated that the NCO— group of TDI or H_{12}MDI had fully reacted with the OH— group of dimethacrylate. Their formulae are presented in Figs. 1 and 2.

For the control group, DM was mixed with dimethacrylate and 20 wt.% tripropylene glycol diacrylate (TPGDA; Double Bond Chemical Ind. Co. Ltd.) as a diluent. The urethane-modified dimethacrylate resin matrices were synthesized using a mixture of dimethacrylate, HEMA, and H_{12}MDI (or TDI) with molar ratios of 1:0.25:0.25, 1:0.5:0.5, 1:1:1, and 1:1.5:1.5. All experimental groups—DM-H-0.25, DM-H-0.5, DM-H-1.0, DM-H-1.5, DM-T-0.25, DM-T-0.5, DM-T-1.0, and DM-T-1.5, and DM-0 as the control group—are listed in Table 1. The urethane-modified resin matrices were added to a 20 wt.% TPGDA diluent monomer. All groups of the resin matrix were then added to 1 wt.% camphorquinone (Acros Chemical Co.), 0.5 wt.% ethyl 4-dimethylaminobenzoate (Acros Chemical Co.), and 50 wt.% silanized silica fillers (average 1.6 μm; Sibelco Bao Lin Co. Ltd., Taichung, Taiwan), and mixed well using a planetary mixer (Kurabo, Mazerustar, KK-250S, Osaka, Japan) to form the composite resins.

Viscosity of resin matrices

The viscosity of resin matrices was measured using a viscometer (Brookfield Engineering Laboratories, Middleboro, MA, USA) at 25°C.

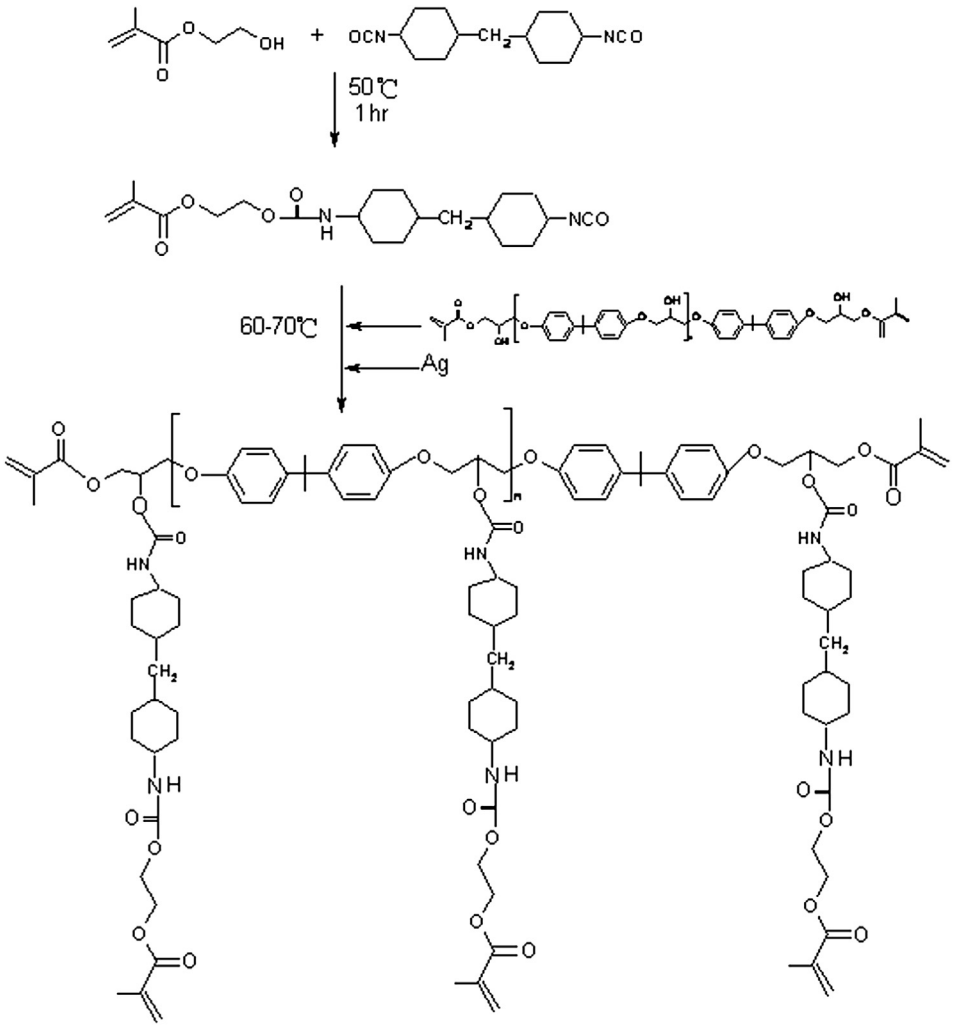

Figure 1 Synthesis of the urethane [4,4′-diisocyanatodicyclohexylmethane (H_{12}MDI)]-modified dimethacrylate.

Polymerization shrinkage

Post-gel polymerization shrinkage was evaluated using a strain gauge method ($n = 5$) as described previously.[7] The experimental composite resins were filled into a cylinder silicone mold (6-mm diameter and 1-mm thickness) on an uniaxial strain gauge (EA-06-062AQ-350/LE; Vishay Micro-Measurements, Shelton, CT, USA) and covered with a transparent Mylar strip. The light curing tip was positioned 1 mm above the composite resin sample and the sample was cured in a continuous mode using an Optilux 501 (Kerr, Danbury, CT, USA) for 180 seconds. Shrinkage data were collected using a Vishay Micro-Measurements Strain Smart 5000 series for 10 minutes from the initiation of light irradiation.

Surface hardness

Experimental composite resins were filled into a silicone mold (6-mm diameter and 1-mm thickness) and covered with a transparent Mylar strip before light curing for 180 seconds. Five indentations were performed on the top surface of each specimen using a Micro Hardness Tester (HMV-2; Shimadzu, Kyoto, Japan), and the average value was obtained. Five specimens of each group were prepared, and the final average value and standard deviation was recorded.

Degree of conversion

The degree of conversion was measured and calculated using a Fourier transform infrared spectrometer (JASCO FT/IR-4200, Tokyo, Japan) ($n = 5$). The composite resin specimens were prepared as described in the "Surface hardness" section. The FTIR spectra of uncured and cured specimens were recorded using an Attenuated Total Reflectance (ATR) device in the following conditions: 2000 to 1000 cm^{-1} wavelength, 4 cm^{-1} resolution, 16 scans coaddition. The FTIR spectra were collected 72 hours after light curing of the specimens. The degree of conversion was calculated using the ratio of two peaks (aliphatic C=C at 1638 cm^{-1} and aromatic C=C at 1608 cm^{-1}). The intensities of the peaks, as ratios of the cured and uncured experimental composite resins, were calculated as described previously.[8] The degree of conversion was expressed as a percentage relative to the uncured status.

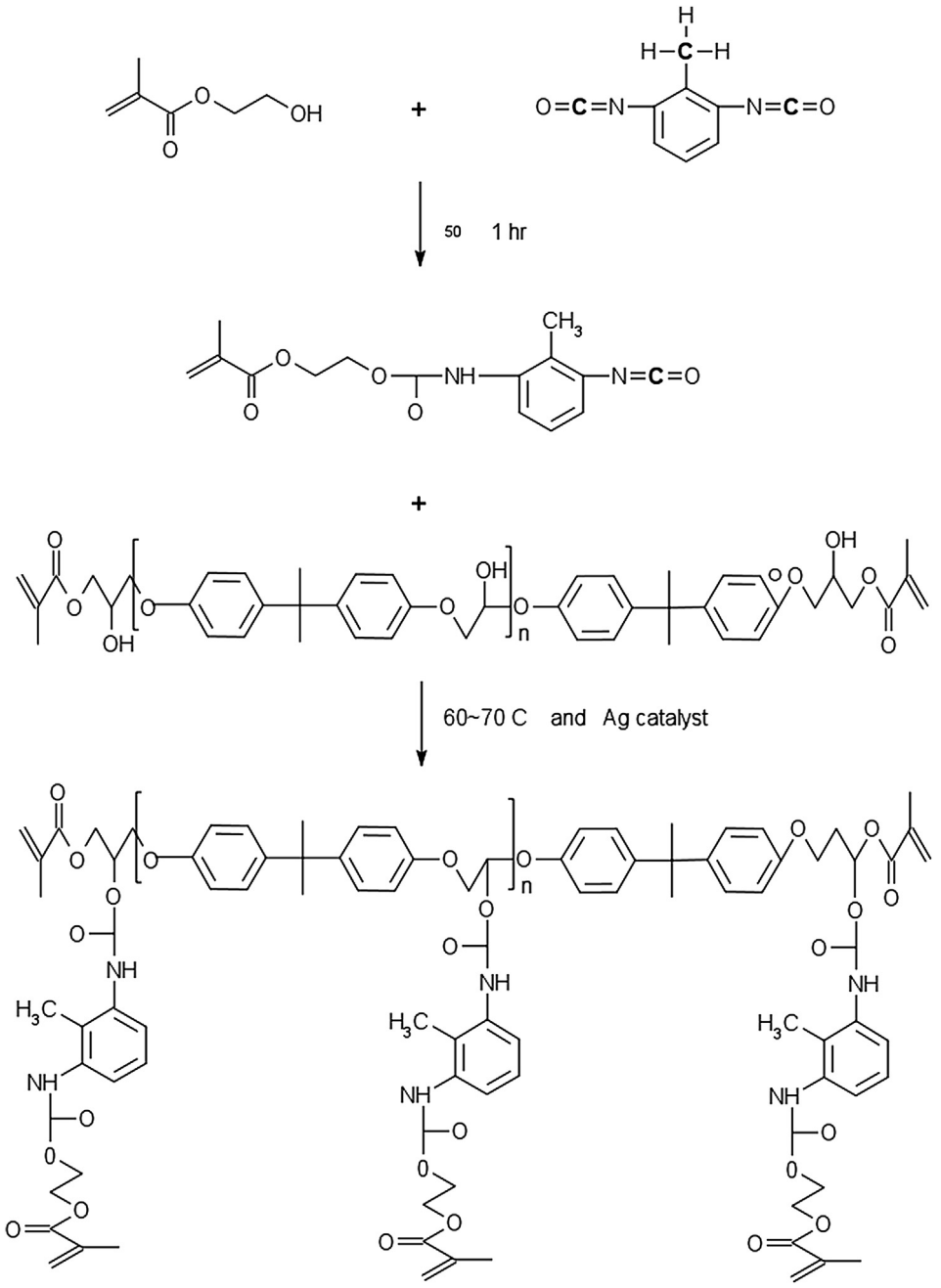

Figure 2 Synthesis of the urethane [toluene 2,4-diisocyanate (TDI)]-modified dimethacrylate.

Statistical analysis

One-way analysis of variance and the Tukey—Kramer *post hoc* test were used to analyze data ($\alpha = 0.05$). Statistical analyses were performed using StatView 5.0 software (SAS Institute, Cary, NC, USA).

Results

Figs. 3,4 and 5 present the polymerization shrinkage, surface hardness, and degree of conversion results, respectively. Table 2 displays the average values and standard deviations of polymerization shrinkage (microstrain), surface hardness (HV), and degree of conversion (%) as well as the molecular weights and viscosities (cPs) of resin matrices. After mixing 50 wt.% silanized silica fillers into the matrix, we evaluated the polymerization shrinkage, surface hardness, and degree of conversion of composite resins. With increasing side chain modification, the polymerization shrinkage remained the same or decreased. Polymerization shrinkage in the DM-H-1.5 and DM-T-1.5 groups was significantly less extensive than in the other groups ($p < 0.05$). The surface hardness of the DM-H-0.25 and DM-H-0.5 groups was significantly higher than that of the control group (DM-0, $p < 0.05$). In all TDI groups, the surface hardness was also significantly higher than that of the control group (DM-0, $p < 0.05$). When comparing the degree of conversions of the H_{12}MDI groups

Table 1 The compositions and ratios of dimethacrylate (DM), 2-hydroxyethyl methacrylate (HEMA), and 4,4′-diisocyanatodicyclohexylmethane (H_{12}MDI) (or toluene 2,4-diisocyanate, TDI) in all experimental dental composite resin groups.

Group/Abbreviation	Composition (wt.%)	
	Resin matrix	Filler
DM-0	DM + tripropylene glycol diacrylate 20% + ethyl 4-dimethylaminobenzoate 0.5% + camphorquinone 1%	50% silanized silica fillers
DM-H-0.25	DM-0 + HEMA + H_{12}MDI DM/HEMA/H_{12}MDI = 1:0.25:0.25	
DM-H-0.5	DM-0 + HEMA + H_{12}MDI DM/HEMA/H_{12}MDI = 1:0.5:0.5	
DM-H-1.0	DM-0 + HEMA + H_{12}MDI DM/HEMA/H_{12}MDI = 1:1:1	
DM-H-1.5	DM-0 + HEMA + H_{12}MDI DM/HEMA/H_{12}MDI = 1:1.5:1.5	
DM-T-0.25	DM-0 + HEMA + TDI DM/HEMA/TDI = 1:0.25:0.25	
DM-T-0.5	DM-0 + HEMA + TDI DM/HEMA/TDI = 1:0.5:0.5	
DM-T-1.0	DM-0 + HEMA + TDI DM/HEMA/TDI = 1:1:1	
DM-T-1.5	DM-0 + HEMA + TDI DM/HEMA/TDI = 1:1.5:1.5	

with that of the control group, we observed a significantly lower degree of conversion in the DM-H-1.0 and DM-H-1.5 groups ($p < 0.05$). When comparing the degree of conversions of the TDI groups with that of the control group, we found a significantly higher degree of conversion in the DM-T-0.25 and DM-T-0.5 groups ($p < 0.05$) and a significantly lower degree of conversion in the DM-T-1.5 group ($p < 0.05$).

The differences in polymerization shrinkage between the H_{12}MDI and TDI groups with the same side chain density were not significant ($p > 0.05$). The surface hardness of the TDI groups was equal to or significantly higher than that of the H_{12}MDI groups ($p < 0.05$). The degree of conversions of the TDI groups was equal to or significantly higher than that of the H_{12}MDI groups ($p < 0.05$). The molecular weights and viscosities of resin matrices elevated with increasing density of the diisocyanate side chains of H_{12}MDI or TDI. The viscosities of the DM-H-1.5 and DM-T-1.5 groups were too high to measure ($>1 \times 10^6$ cPs).

Discussion

In this study, we synthesized resin matrices using dimethacrylate as the main structural component, and HEMA and diisocyanate, in various proportions, as conjugated side chains. With increasing side chain density on dimethacrylate, the volumes of the monomer molecules and the molecular weights increased. The hydrogen bonds between

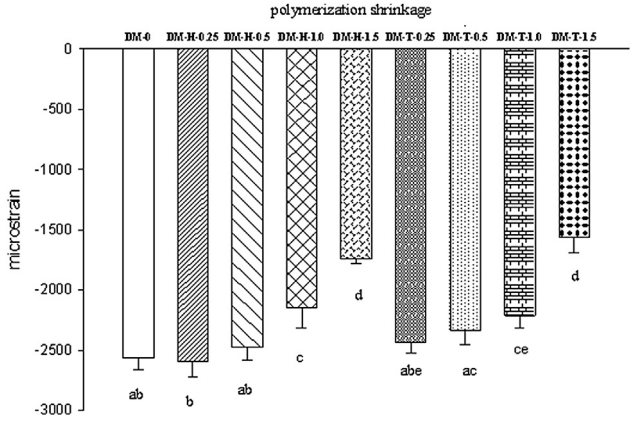

Figure 3 Polymerization shrinkage of the control, H_{12}MDI-, and TDI-modified resin matrix groups. If two different groups carry the same letter, then there is no significant difference between the two groups ($p > 0.05$); otherwise there is a significant difference between the two groups ($p < 0.05$).

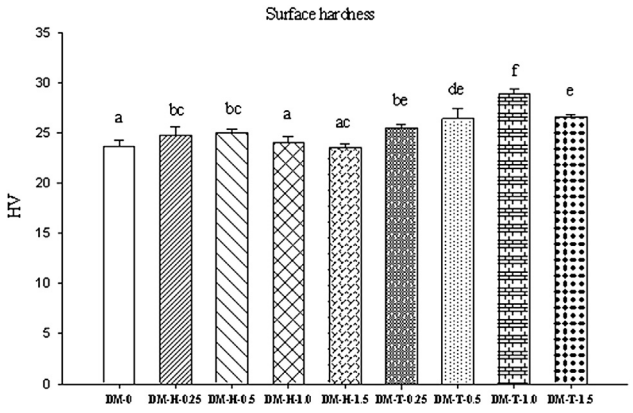

Figure 4 Surface hardness of the control, H_{12}MDI-, and TDI-modified resin matrix groups. If two different groups carry the same letter, then there is no significant difference between the two groups ($p > 0.05$); otherwise there is a significant difference between the two groups ($p < 0.05$).

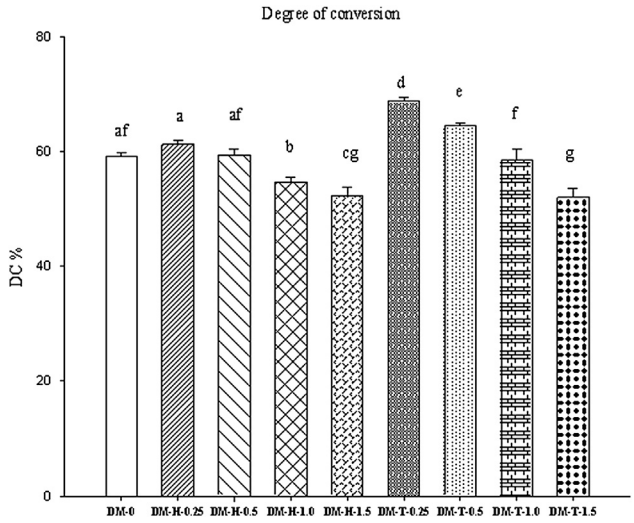

Figure 5 Degree of conversion of the control, H_{12}MDI-, and TDI-modified resin matrix groups. If two different groups carry the same letter, then there is no significant difference between the two groups ($p > 0.05$); otherwise there is a significant difference between the two groups ($p < 0.05$).

the urethane groups also increased. The presence of intermolecular hydrogen bonds explained the observation of increasing viscosity with increasing side chain modification. It is therefore possible to modify the side chain density on dimethacrylates to control the viscosity of the resin matrix and to increase its suitability for application in restorative composite resins or flowable resins.

The strain gauge method is a powerful and appropriate method for measuring the post-gel polymerization shrinkage of composite resins.[9] In this study, polymerization shrinkage was reduced significantly in DM-H-1.0, DM-H-1.5, DM-T-1.0, and DM-T-1.5 groups compared to the control group. These results indicate the need for a higher side chain density when using the side chain modification method to reduce polymerization shrinkage. Polymerization shrinkage in the DM-H-1.5 (−1744.6 microstrain) and DM-T-1.5 (−1564.8 microstrain) groups was significantly lower than in all other groups, and these values were also lower than those of commercial flowable composite resins.[10] Although the degree of conversions of these two groups were significantly lower than that of the control group, the surface hardness values were equal to or significantly higher than that of the nonmodified dimethacrylate (control) group because of increasing functionalities of the side chain-modified groups. In side chain-modified groups, the degree of conversion decreased when the side chain density increased because of increasing viscosity and steric hindrance. With increasing viscosity and steric hindrance of composites, the motions of the monomers and the intermolecular reactions were reduced. This results in a decrease in cytotoxicity because the resin monomer is the main ingredient of dental composite resin causing the cytotoxicity. Polymerization shrinkage and degree of conversion are antagonistic goals of composite resins. Generally, increased monomer conversion results in more extensive polymerization shrinkage. Composite resins with lower conversion might, therefore, display more reduced polymerization stress than those with higher conversion.[11] However, in lower conversion composite resins, the mechanical properties, biocompatibility, and longevity of restorations are of concern. In polymer cross-linking systems, unreacted double bonds in the polymer are not necessarily free of monomers, but could also result from pendant double bonds that are tied into the polymer network.[12] An ideal dental composite resin would, therefore, have minimal polymerization shrinkage and an optimal degree of conversion.[13] In this study, the polymerization shrinkage of all groups was equal to or significantly lower than that of the nonmodified control group, and the surface hardness of these groups was also equal to or significantly higher than that of the control group, despite some groups' degree of conversion being marginally lower than that of the control group. The degradation and biocompatibilities of composite resins are other issues that deserve further investigations.

In this study, we modified bisphenol A dimethacrylate using side chains of two different structures: two cyclohexane rings (C_6H_{12}) in H_{12}MDI and a benzene ring (C_6H_6) in TDI. Different side chain structures might result in different composite resin properties. In groups with the same side chain density, the differences in polymerization shrinkage

Table 2 The average values and standard deviations of polymerization shrinkage (microstrain), surface hardness (HV), and degree of conversion (%) as well as the molecular weights and viscosities (cPs) of experimental composite resins. Data are presented as mean (standard deviation).

Composite resin group	Shrinkage (microstrain)	Hardness (HV)	Degree of conversion (%)	Molecular weight	Viscosity (cPs)
DM-0	−2563.4 (94.0)^{a,d}	23.7 (0.6)^{a}	59.1 (0.8)^{a,f}	512.6	3522
DM-H-0.25	−2593.0 (133.5)^{a}	24.8 (0.8)^{b,c}	61.3 (0.6)^{a}	610.6	30,808
DM-H-0.5	−2476.0 (110.8)^{a,d}	25.0 (0.3)^{b,c}	59.4 (1.0)^{a,f}	708.6	248,000
DM-H-1.0	−2143.4 (171.8)^{b,e}	24.0 (0.7)^{a}	54.7 (0.8)^{b}	904.6	556,000
DM-H-1.5	−1744.6 (33.2)^{c}	23.6 (0.3)^{a,c}	52.3 (1.7)^{c,g}	1100.6	>1,000,000
DM-T-0.25	−2431.4 (87.6)^{a,d,f}	25.5 (0.4)^{b,e}	68.8 (0.8)^{d}	588.6	53,678
DM-T-0.5	−2338.6 (112.0)^{d,e}	26.4 (1.0)^{d,e}	64.6 (0.4)^{e}	664.7	195,000
DM-T-1.0	−2213.0 (102.8)^{e,f}	28.9 (0.4)^{f}	58.6 (1.8)^{f}	816.8	869,000
DM-T-1.5	−1564.8 (122.3)^{c}	26.6 (0.3)^{e}	52.1 (1.6)^{g}	968.8	>1,000, 000

$^{a, b, c, d, e, f}$ If two different groups carry the same letter, then there is no significant difference between the two groups ($p > 0.05$); otherwise there is a significant difference between the two groups ($p < 0.05$).

between the H_{12}MDI- and TDI-modified groups were nonsignificant. The surface hardness of the TDI-modified groups was equal to or higher than that of the H_{12}MDI-modified groups. H_{12}MDI contains two aliphatic rings (cyclohexane) linked by a methyl group, and confers a softer chemical structure than TDI, which contains a toluene moiety. The TDI-modified groups thus demonstrated greater surface hardness values. The degree of conversions of the TDI-modified groups was higher than that of the H_{12}MDI-modified groups except that of the DM-T-1.5 group. The molecular weights and steric hindrance of the H_{12}MDI-modified groups were higher than those of the TDI-modified groups, and the motions and reactivities of the H_{12}MDI groups were lower than those of the TDI groups. The degree of conversions of the H_{12}MDI groups was, therefore, lower than that of the TDI groups. In groups with the same side chain density, the molecular weights and steric hindrance of the H_{12}MDI groups were higher than those of the TDI groups; however, the properties of the H_{12}MDI groups were not superior to those of the TDI groups for use in composite resins. We conclude that using side chains with optimal molecular weights and steric hindrance can result in composite resins with optimal properties.

In this study, we synthesized new dental resin matrices using a mixture of diisocyanate (H_{12}MDI or TDI), HEMA, and bisphenol A dimethacrylate in differing ratios. According to the density of the modifying side chains, the viscosity of the matrix could be controlled to form flowable or restorative composite resins. With increasing diisocyanate side chain density, the polymerization shrinkage of the composite resins reduced and the surface hardness increased compared to the nonmodified control group. The urethane modification of dimethacrylate, therefore, represents an effective means of reducing polymerization shrinkage and increasing surface hardness. Future investigations should include evaluations of biocompatibility and mechanical properties of these urethane-modified dental composite resin matrices, such as flexural strength, modulus of elasticity, wear resistance, and cytotoxicity.

Acknowledgments

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